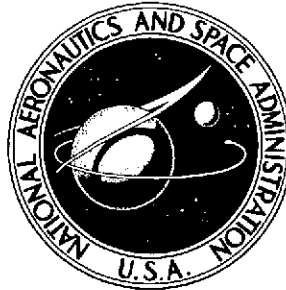


NASA TECHNICAL NOTE



NASA TN D-7933

NASA TN D-7933

(NASA-TN-D-7933) REACTION OF SULFUR DIOXIDE
WITH MODIFIED 440C, STUDIED BY AUGER
ELECTRON SPECTROSCOPY AND DEPTH PROFILING
(NASA) 23 p HC \$3.25 CSCL 11F

N75-18399

Unclas
H1/26 12838

REACTION OF SULFUR DIOXIDE
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BY AUGER ELECTRON SPECTROSCOPY
AND DEPTH PROFILING

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1. Report No. NASA TN D-7933		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle REACTION OF SULFUR DIOXIDE WITH MODIFIED 440C, STUDIED BY AUGER ELECTRON SPECTROSCOPY AND DEPTH PROFILING				5. Report Date March 1975	
				6. Performing Organization Code	
7. Author(s) John Ferrante				8. Performing Organization Report No. E-8175	
				10. Work Unit No. 506-16	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Note	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract Auger electron spectroscopy (AES) and sputtering were used to study the interaction of SO ₂ with modified 440C, which is a nominally 77-wt%-Fe, 14-wt%-Cr, and 4-wt%-Mo bearing steel with C, S, Si, Ni, V, P, and Mn making up the balance. The sample was polycrystalline. Chemical reactions were performed at a pressure of 10 ⁻⁵ torr. Three temperatures were used: room temperature, 500 ^o C, and 600 ^o C. The reaction time was varied from 30 minutes to 2 hours. A surface cleaned of oxides was the starting point for each reaction. For reactions at 500 ^o C the major constituents Cr, O, Fe, and S were present in the surface film. At 600 ^o C the principal constituents of the film were Cr, O, and S with no Fe present. Therefore, a transition in film composition occurred between 500 ^o and 600 ^o C. Oxides were the primary constituents of the films at both temperatures. Room-temperature reactions indicated that SO ₂ adsorbed dissociatively, with approximately equal quantities of S and O on the surface. For the same reaction time (1 hr) and a pressure of 10 ⁻⁵ torr, a strong temperature dependence of film thickness was observed. The film formed at 600 ^o C was approximately seven times thicker than that formed at 500 ^o C.					
17. Key Words (Suggested by Author(s)) Alloy steel Sulfur dioxide Oxidation Sulfidation Depth profiling				18. Distribution Statement Unclassified - unlimited STAR category 26 (rev.)	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 22	
				22. Price* \$3.25	

* For sale by the National Technical Information Service, Springfield, Virginia 22151

REACTION OF SULFUR DIOXIDE WITH MODIFIED 440C,
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AND DEPTH PROFILING

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SUMMARY

Auger electron spectroscopy (AES) and sputtering were used to study the interaction of sulfur dioxide (SO_2) with modified 440C, which is a nominally 77-weight-percent-iron (Fe), 14-weight-percent-chromium (Cr), and 4-weight-percent-molybdenum (Mo) bearing steel with carbon (C), sulfur (S), silicon (Si), nickel (Ni), vanadium (V), phosphorous (P), and manganese (Mn) making up the balance. The sample was polycrystalline. Chemical reactions were performed at a pressure of 10^{-5} torr. Three temperatures were used: room temperature, 500°C , and 600°C . The reaction time was varied from 30 minutes to 2 hours. A surface cleaned of oxides was the starting point for each reaction. For reactions at 500°C the major constituents Cr, O, Fe, and S were present in the surface film. At 600°C the principal constituents of the film were Cr, O, and S with no Fe present. Therefore, a transition in film composition occurred between 500°C and 600°C .

Oxides were the primary constituents of the films at both temperatures. Room-temperature reactions indicated that SO_2 adsorbed dissociatively, with approximately equal quantities of S and O on the surface. For the same reaction time (1 hr) and a pressure of 10^{-5} torr, a strong temperature dependence of film thickness was observed. The film formed at 600°C was approximately seven times thicker than that formed at 500°C .

INTRODUCTION

Sulfur and oxygen and their reaction product sulfur dioxide (SO_2) are important in boundary lubrication of metals (refs. 1 to 3). In addition, SO_2 is a corrosive gas present in the atmosphere (refs. 3 to 6). Therefore, it is important to gain an understanding

of how SO_2 interacts with metals that are present in mechanical equipment, such as bearing steels. Most studies performed with SO_2 as a reactant gas have used metal surfaces covered with oxides as a starting point. Few studies have been performed with a well-defined analysis of surface composition as a starting point.

In the past 10 years, new tools have been developed for examining surfaces. Auger electron spectroscopy (AES) is a technique described in reference 7 for examining the elemental composition and, in some cases, the compound composition to a depth of four or five atomic layers. In addition, sputtering, a method described in reference 8 for removal of material from a surface by positive ion bombardment, is a useful tool for surface cleaning. These tools have been used in combination to obtain depth profiles of surface composition (ref. 9).

In the present study the interaction of SO_2 with 440C, an Fe-Cr alloy widely used as a bearing material, at elevated temperatures was examined by using depth profiling. The study had two main purposes: first, to provide information of value in understanding the interaction of SO_2 with bearing materials under controlled conditions; and second, to compare results with those previously observed in the oxidation of modified 440C (ref. 10).

In this investigation the reaction of modified 440C was examined at a pressure of 10^{-5} torr and at room temperature, 500°C , and 600°C . The interaction time of SO_2 with 440C was varied from 30 to 120 minutes in order to determine the time-dependent composition of surface films. The starting point of each interaction was a surface cleaned of oxides. Following interactions, depth profiles of surface composition were obtained. These results were then compared with oxidation studies performed on the same alloy (ref. 10).

MATERIALS, APPARATUS, AND PROCEDURE

Materials

The sample of polycrystalline, modified, 440C steel was cut from materials used in friction experiments. Its nominal composition in weight percent was 13 to 15 Cr, 0.75 Ni (max.), 0.15 V (max.), 0.1 Mn (max.), 1 Si (max.), 1 to 1.2 C, 3.75 to 4.25 Mo, 0.035 P (max.), 0.025 S (max.), and the balance Fe.

Research-grade argon (Ar) was used for sputtering, in obtaining depth profiles, and for surface cleaning. Research-grade SO_2 was used for the gas-solid interaction studies.

Sample Preparation

The sample studied was a cylinder approximately 1 centimeter in diameter and 0.5 centimeter thick. The specimen was polished with varying grades of silicon carbide paper to a 600-grit finish. It was then polished with 3-micrometer-diamond paste and given a final polish with 1-micrometer alumina. In preparing the surface for cleaning, the sample was outgassed at 700° C and cooled slowly to produce an annealed specimen.

Apparatus

The vacuum system was a bakeable, 250° C, stainless-steel, ultra-high-vacuum system. The chamber was evacuated by sorption, sublimation, and ion pumps. The base pressure for the system was 10^{-10} torr as measured with a nude Bayard-Alpert gage. The sample was heated by electron bombardment and radiation. Sample temperature was measured with a Chromel-Alumel thermocouple spot welded to its shank. The AES system used was a standard retarding-field analyzer shown schematically in figure 1.

Experimental Procedure

Several initial steps were pursued in preparing the sample for chemical reaction. The specimen was outgassed at 700° C until the pressure in the vacuum system could be maintained in the 10^{-10} -torr range at temperature with all filaments heated. The sample was then cleaned by argon ion bombardment at 2 kilovolts and $3.5 \mu\text{A}/\text{cm}^2$. A typical AES spectrum following argon ion bombardment and then annealing at 700° C for 30 minutes is shown in figure 2. In all cases P, S, and nitrogen (N) segregated at the surface upon annealing. The AES spectrum of a surface that had reacted with SO_2 at 500° C and 10^{-5} torr for 1 hour is shown in figure 3. The size of the S peak shown following reaction with SO_2 is large (fig. 3) compared to that following cleaning and annealing (fig. 2).

A series of studies were performed involving adsorption, heating in SO_2 , and examining the composition of the resultant surface film by depth profiling. The general procedure followed for the adsorption and SO_2 -metal interaction studies was first to sputter clean the surface and then to anneal at 700° C for 30 minutes in all cases before exposing the surface to SO_2 . The surface was then exposed to SO_2 at a pressure of 10^{-5} torr. The sample was exposed at room temperature, 500° C, 600° C, and 700° C. Following heating in SO_2 , surface depth profiles were obtained by observing the appropriate portion of the AES spectrum during argon ion bombardment.

In order to obtain depth profiles of the surface oxide films, the sample was bombarded with argon ions at $3.5 \mu\text{A}/\text{cm}^2$ and 2 kilovolts while AES spectra were simultaneously taken. In all these studies the sample was heated in SO_2 at the same pressure (10^{-5} torr). At lower pressures the SO_2 sticking coefficient was too low to form surface films at temperatures above room temperature (500° , 600° , and 700° C). It should be noted that the Bayard-Alpert gage has a higher sensitivity to SO_2 than to oxygen by a factor of 2.3 (ref. 11). Therefore, for an equivalent pressure of oxygen there is a lower SO_2 arrival rate. The pressure of 10^{-5} torr was also a practical upper limit of pressure for the vacuum system with the pump on. Two surface temperatures (500° and 600° C) were used in forming the surface films. At 700° C and a pressure of 10^{-5} torr, no film was formed - the SO_2 sticking coefficient was too low to form a surface film. The sample was heated for 60 or 120 minutes at 500° C and for 30 or 60 minutes at 600° C in order to establish the effect of reaction time on film composition. Following processing of the steel sample under these conditions, compositional depth profiles were taken. Shorter reaction times were used at 600° C because the thicker films formed would require excessively long sputtering times. In these cases the sample was not moved; therefore, the results represent analysis at the same spot on the surface. However, several spots on the surface were examined to establish that the results were not local. In order to estimate the time needed to sputter a layer of SO_2 film, the surface was exposed to SO_2 for 30 minutes at room temperature and a pressure of 10^{-5} torr. This was sufficient time for saturation of the oxygen and sulfur peak-to-peak heights, and the result was assumed to represent one layer of surface film.

The principal AES peaks observed for these studies were the S(150 eV), O(511 eV), Cr(487 eV), Cr(527 eV), Fe(596 eV), Fe(646 eV), and Fe(702 eV). However, in all cases the spectrum from 100 to 1000 electron volts was checked for effects from other alloying materials.

In order to ensure SO_2 purity during exposure, the ion pump was given repeated argon instability treatments (ref. 12). The ion pump was operating during all SO_2 exposures. Composition of the SO_2 bled into the vacuum system was checked with a quadrupole mass spectrometer. A typical mass spectrometer trace taken at a pressure of 10^{-5} torr with the ion pump on is shown in figure 4. The primary constituents from the SO_2 are 16 (O), 32 (S), 48 (SO), and 64 (SO_2). The primary contaminant is 40 (Ar). The cracking pattern for SO_2 (ref. 11) differs from the ratios given in figure 4. However, the sensitivity of a quadrupole mass spectrometer decreases with mass number for high resolution. As a check, a mass spectrum was taken shortly after the ion pump was turned off to establish if cracking were occurring in the pump. The mass ratios remained substantially the same, indicating that the pump was not causing cracking of the SO_2 . The AES electron gun was off during all exposures. The AES data for the Fe, O, Cr, and S depth profiles were obtained after two separate exposures. In presenting the data from the depth profiles, the peak heights represent raw data, with the exception

of sulfur. For sulfur the peaks were divided by the relative AES sensitivities of sulfur to oxygen as presented by Meyer and Vrakking (ref. 13), who determined the sulfur sensitivity by using hydrogen sulfide (H_2S). Therefore, the ratios of the sulfur to oxygen peaks presented represent ratios of atomic concentrations.

RESULTS

In order to calibrate for surface thickness, the metal surface was exposed to SO_2 at 10^{-5} torr for 30 minutes to guarantee saturation at room temperature. The results of this adsorption and subsequent depth profiling are shown in figure 5. It took a sputtering time of 9 minutes for the oxygen peak to disappear into the AES background and 6 to 7 minutes for it to be reduced to 10 percent of its initial value. This information can be used to provide a rough estimate of the number of layers sputtered in subsequent data.

Figures 6 to 11 show the results of heating the surface in SO_2 under two different conditions and then depth profiling the subsequent surface films. The conditions were an SO_2 pressure of 10^{-5} torr and a temperature of either 500°C for 60 or 120 minutes or 600°C for 30 or 60 minutes. The film for each figure is denoted by the region of the material containing oxygen. The region up to the break in oxygen concentration will be referred to as the outer layer. The tailoff of the oxygen peak in these figures is a real physical effect rather than an artifact of the sputtering since only 9 minutes of sputtering were required to completely remove oxygen following monolayer adsorption.

The results for the 500°C reactions are shown in figures 6 to 8. For both reaction times, Fe, Cr, O, and S were present in the films. The film for the longer exposure was thicker, as expected. The sulfur concentration was higher in the surface layers than in the bulk. The iron concentration was higher in the 1-hour-exposure film than in the 2-hour film. The surface layer of the longer exposure film had a lower oxygen concentration. Figure 8 shows the oxygen concentration against depth for the two heating times in order to give a comparison of the relative thickness. All major elements in the alloy and in the SO_2 were present in the film after heating at 500°C .

The results of reacting at 600°C for 30 or 60 minutes are shown in figures 9 to 11. These results differ from those at 500°C in that Fe was absent. The surface film contained only Cr, O, and S. Figure 10 for the 60-minute exposure shows sulfur behavior similar to that at 500°C ; that is, the surface layer was rich in sulfur. There is more oxygen and chromium in the film below the sulfur-rich surface layer. In the outer layer the oxygen-to-sulfur atom ratio is large (10:1). Although the sulfur peak was not monitored for the 30-minute exposure, its behavior is expected, from the trends in the oxygen and chromium peaks, to be similar to that for the 60-minute exposure. Again the film is thicker after the longer exposure. The composition of the film in these cases

seems to be largely chromium oxides. The shorter-exposure curves indicate a small iron concentration in the outer layers. Figure 11 shows the magnitude of the oxygen peaks plotted on the same time base in order to give a relative comparison of film thickness.

Figure 12 shows depth profiles of the oxygen peak taken under two conditions - 500°C and 10^{-5} torr, and 600°C and 10^{-5} torr - for the same reaction time (1 hr). This figure provides an example of the effect of temperature on film thickness.

DISCUSSION

The purpose of the present study was twofold: first, to examine what effects the presence of sulfur would have on film formation in a bearing metal, since sulfur is an important additive in many bearing applications; and second, to serve as an independent verification of the result observed in reference 10 that there was a transition temperature above which the outer film contained no iron. With these main objectives, therefore, the interaction of SO_2 with 440C was pursued.

Composition of Surface Film

In a previous study of the oxidation of modified 440C (ref. 10), it was found that the composition of the outer surface oxide changed from one containing oxygen, iron, and chromium for oxidations performed at 10^{-6} torr and temperatures of 600°C and below to a film containing oxygen and chromium but no iron for oxidations performed at 10^{-6} torr and temperatures of 700°C and above. Similar results were observed in the present study. At a temperature of 600°C and a pressure of 10^{-5} torr the outer film contained no iron and was composed of chromium, oxygen, and sulfur (figs. 9 to 11). At 500°C and below and 10^{-5} torr, all major elements were present in the outer film (figs. 6 to 8). The temperature at which the chromium-rich layer dominated was different from that observed in reference 10. This fact is not necessarily surprising, however, since the presence of sulfur in the film could alter diffusion rates.

Adsorption of Sulfur Dioxide

The adsorption results of this study differ from those of reference 10. In that study when oxygen was adsorbed at room temperature, a definite surface reaction occurred in which the chromium peaks disappeared from the AES spectrum and only iron and oxygen were present. In this study it appears that only adsorption occurred in that no peaks

disappeared from the spectrum but only a reduction in peak height occurred (fig. 5). This result was also true for other peaks in the spectrum; that is, both the molybdenum and carbon peaks were simply reduced in height when the SO_2 was adsorbed. There is evidence that the SO_2 adsorbed dissociatively with one oxygen atom missing from the molecule, in that the oxygen and normalized sulfur peak heights were approximately the same size in figure 5. If we accept the relative sensitivities given by Meyer and Vrakking (ref. 13), the oxygen-to-sulfur ratio was approximately 1:1 rather than 2:1.

Possible Mechanisms for Film Formation

As in the case of oxygen reaction with modified 440C (ref. 10), the results of the present study are quite complicated. It was found that the composition of the surface film varied with temperature. For example, at 700°C the sticking coefficient of SO_2 was too low to form a surface film at 10^{-5} torr. At 500°C , all major components of the alloy and the reacting gas were present in the surface film; at 600°C the film composition was selectively oxides and sulfides of chromium. It is apparent from figures 6 and 10 that the major constituents of the films formed were oxides, if we accept that there is not a large discrepancy between the sputtering yields of oxygen and sulfur. This result is similar to the results of reference 6, wherein SO_2 was reacted with nickel, but differs in that the sulfur-rich layer was at the film surface rather than at the film-metal interface.

The results of the present study indicate that mechanisms similar to those proposed in reference 10 were operating. Two factors affect reaction rate: reactivity and concentration. Depending on the sample temperature, there are two competing phenomena - the reactivity of the constituents making up the film and the rates of diffusion of the film constituents at various temperatures (which affect the concentration in the reaction region). Chromium is the most reactive material of the major components in the alloy, and oxygen is the most reactive component in the reacting gas. The present results can be explained by assuming that chromium diffuses more slowly than iron. At the lower temperatures, although chromium is more reactive, its diffusion rate in the reacting region is sufficiently low that its concentration is low and therefore it does not dominate the formation of the surface film. At higher temperatures the increased diffusion of chromium creates a higher concentration and therefore dominance in the film formation. It is not surprising that oxygen would be the major film constituent since it has a higher reactivity than sulfur and also has a higher arrival rate (two oxygen atoms to one sulfur) at the surface. Coad and Cunningham (ref. 14) came to similar conclusions in examining oxide compositions on iron-chromium alloys.

The effects of reaction time are examined in figures 6 and 7 for heating at 500°C . We can see that the film composition remains substantially the same for the two reaction

times. In figure 8 the oxygen AES peaks are plotted separately for the two reaction times at 500° C in order to indicate the increased film thickness. The films formed increased in thickness with reaction time as expected. Figure 11 also shows the oxygen AES peaks for two reaction times at 600° C in order to demonstrate film growth. The film composition again remained substantially the same for reaction times of 30 and 60 minutes. The main difference was simply film thickness.

Effect of Temperature on Film Thickness

Figure 12 shows a depth profile of the oxygen peak for the same pressure (10^{-5} torr) and the same reaction time (1 hr) but different temperatures (500° and 600° C). It can be seen that there is a strong temperature effect on film thickness. If we take the point at which the oxygen concentration falls to half its maximum value as a measure of film thickness, the film formed at 600° C is approximately seven times thicker than the film formed at 500° C.

The present results support those of reference 10, wherein a temperature dependence on film composition was observed. In fact, in the present study a transition in film composition was observed between 500° and 600° C. The primary metallic constituent of the surface films was chromium at 600° C, with both chromium and iron present at 500° C. The primary nonmetallic component of the surface films was oxygen.

The importance of this study is that it substantiates results obtained in a previous study of the oxidation of 440C and provides additional information in understanding the reaction of active gases with bearing materials. The conditions are also important in that they define conditions for forming desired films under controlled environments and states of surface cleanliness. For example, if an outer layer containing only chromium as a metallic constituent is desired, the conditions are established in this report for obtaining that end. Finally, the time-dependent studies suggest future experiments to examine film growth rates for thick and thin films under controlled conditions.

CONCLUSIONS

Auger electron spectroscopy and sputtering were used to study the interaction of sulfur dioxide with modified 440C. The following conclusions were reached:

1. At 600° C and an ambient sulfur dioxide (SO_2) pressure of 10^{-5} torr for 30- and 60-minute reaction times, surface films whose primary metallic constituent was chromium (Cr) and whose primary nonmetallic constituent was oxygen (O) were formed on 440C. Sulfur (S) was also present in the films.

2. At 500⁰ C and an ambient SO₂ pressure of 10⁻⁵ torr for 60- and 120-minute reaction times, surface films whose constituents were iron (Fe), Cr, O, and S were formed on 440C. Oxygen was present in higher quantities than sulfur in the film.

3. The results agree with those observed in a previous study of the oxidation of 440C in that a transition temperature was observed. For reaction at 500⁰ C the outer layers of the film contained all major elements involved in the reaction; whereas for reaction at 600⁰ C, iron was missing and only chromium was present as the metallic constituent of the outer layer.

4. It can be quantitatively stated that oxides rather than sulfides were the major constituents of the films.

5. Both diffusion rates and chemical reactivity were important in the composition of the surface films formed.

6. Sulfur dioxide adsorbs dissociatively, with sulfur and oxygen present on the surface in a ratio of 1:1 at room temperature, and forms a monolayer-type film.

7. A strong dependence of film thickness on temperature was observed for the same reaction time (1 hr) and the same pressure (10⁻⁵ torr). The film formed at 600⁰ C was approximately seven times thicker than that formed at 500⁰ C.

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, December 30, 1974,

506-16.

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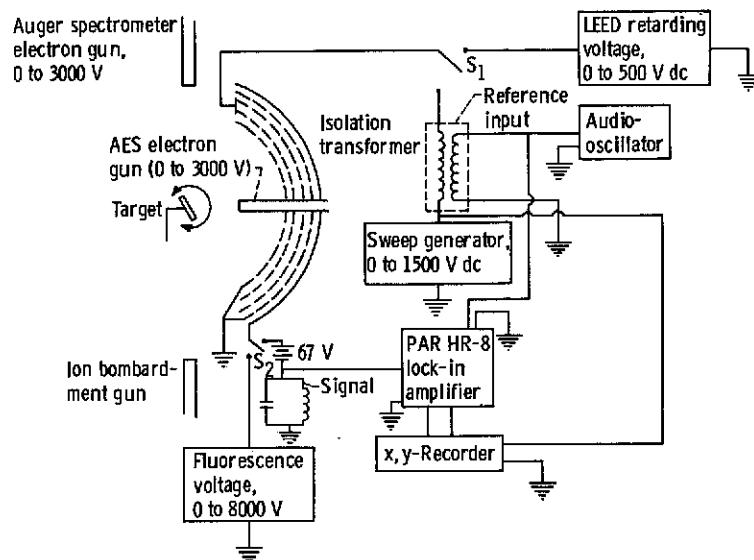


Figure 1. - Schematic diagram of Auger electron spectroscopy (AES) apparatus.

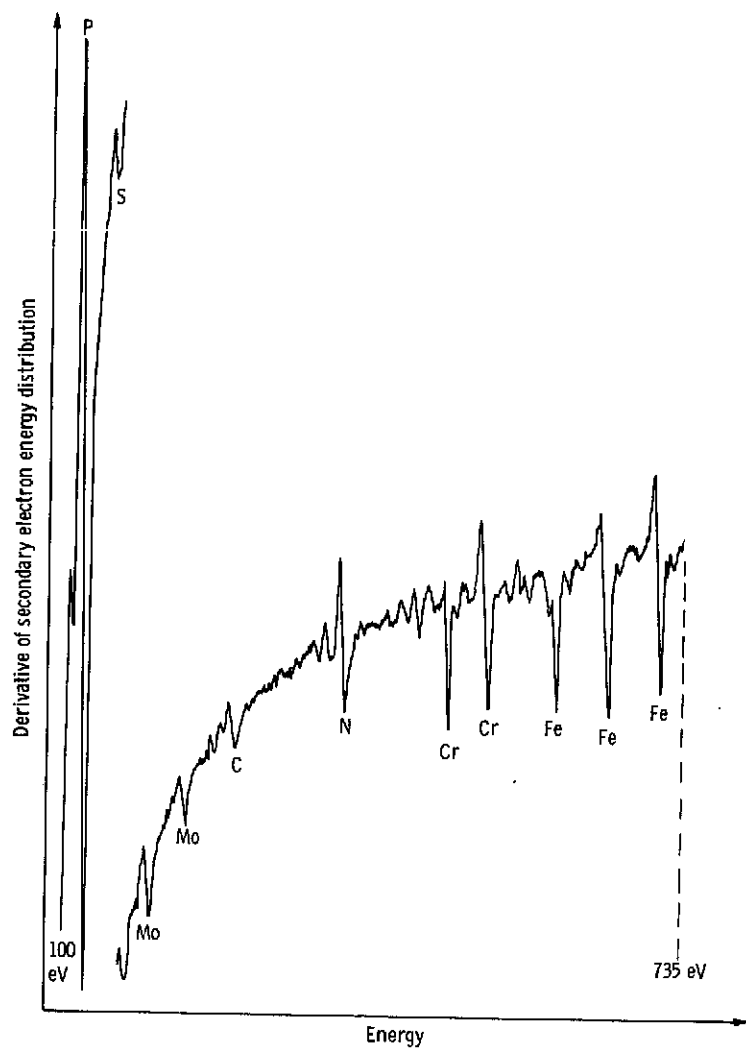


Figure 2. - Typical AES spectrum following annealing for 30 minutes at 700° C after sputter cleaning. (From ref. 10.)

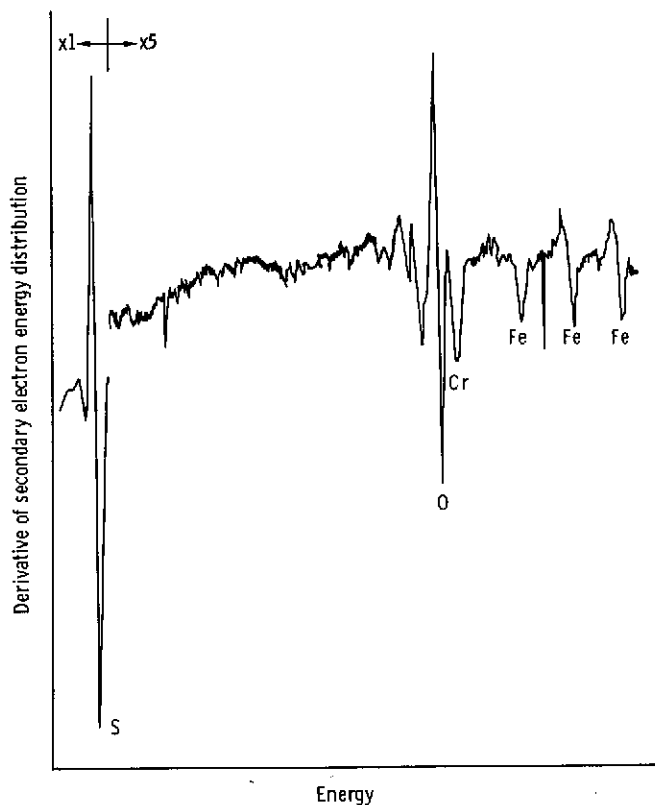


Figure 3. - Typical AES spectrum following heating in SO_2 at 500°C and 10^{-5} torr for 1 hour.

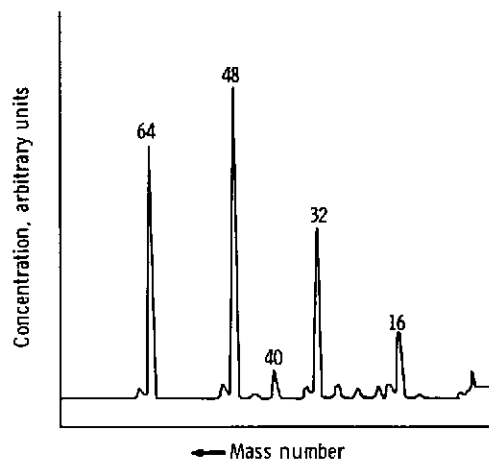


Figure 4. - Quadrupole mass spectrometer trace of gas concentration against mass number for SO_2 admitted to vacuum system at 10^{-5} torr with ion pump on.

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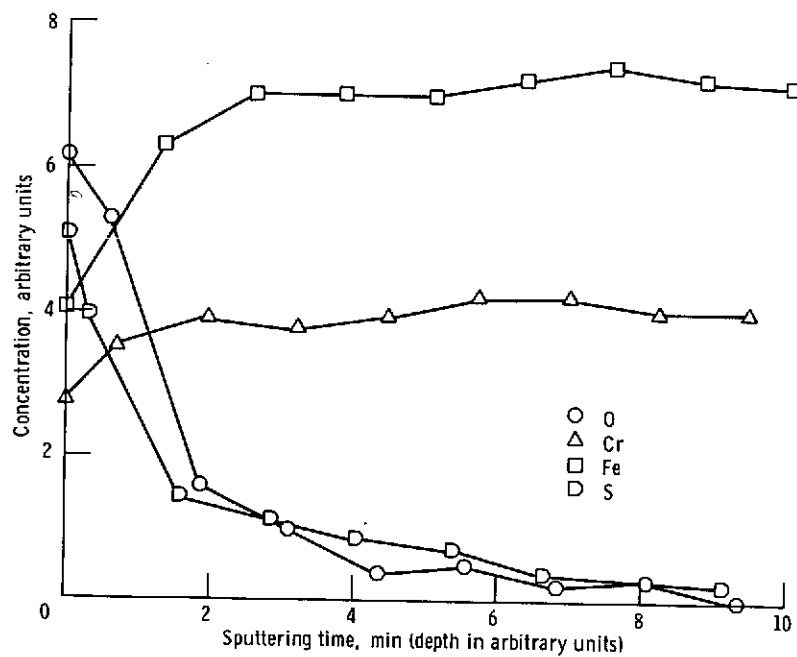


Figure 5. - Depth profile of 440C surface following adsorption of SO_2 at room temperature and 10^{-5} torr for 30 minutes.

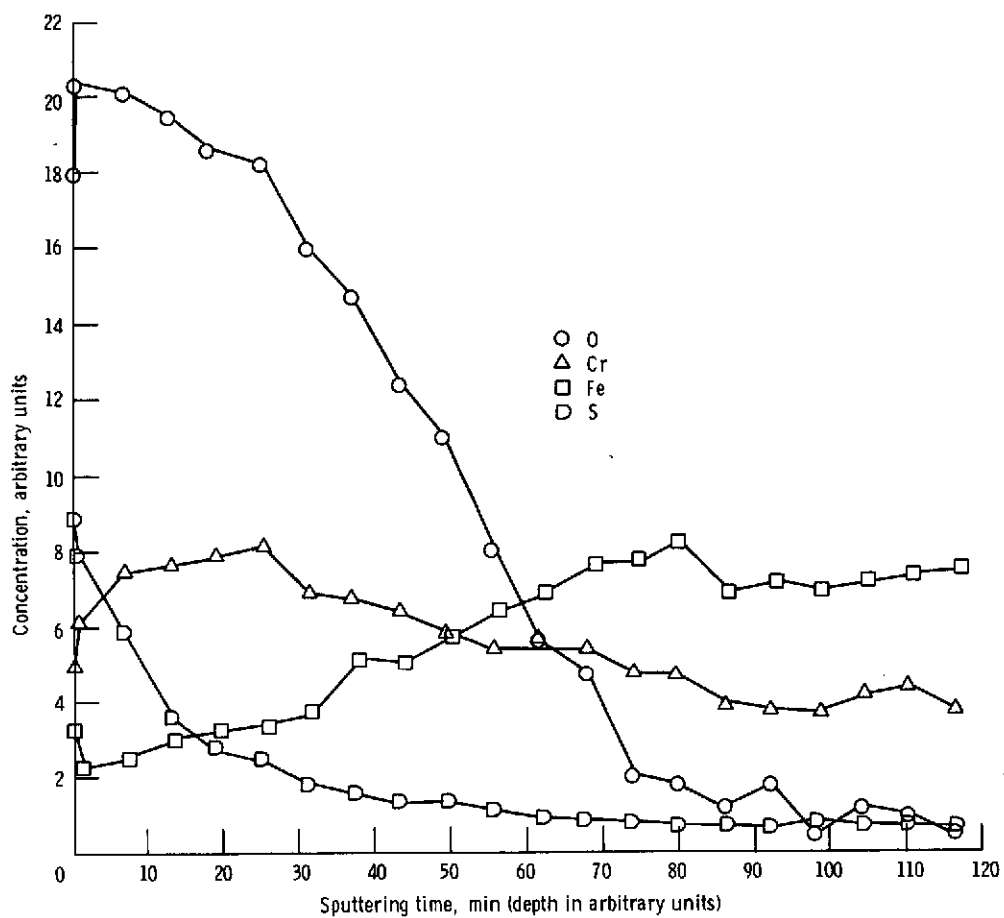


Figure 6. - Depth profile of 440C surface following reaction with SO_2 at 500°C and 10^{-5} torr for 60 minutes.

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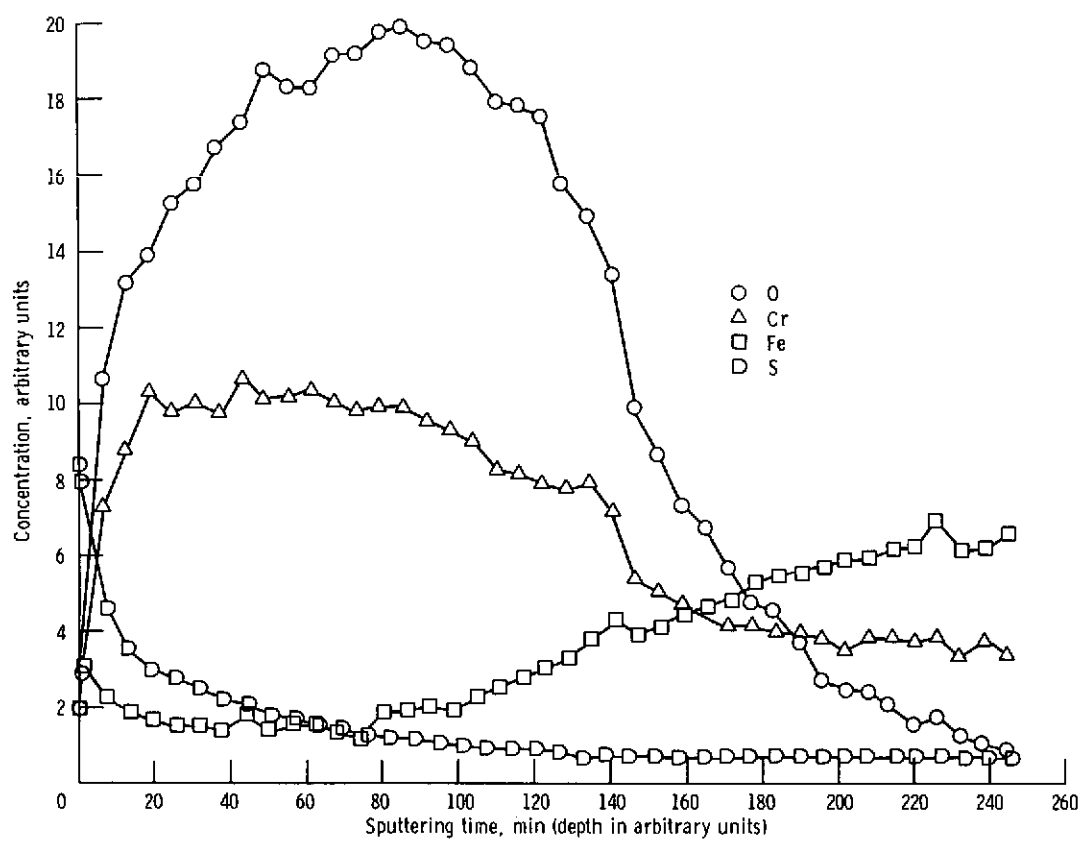


Figure 7. - Depth profile of 440C surface following reaction with SO_2 at 500°C and 10^{-5} torr for 120 minutes.

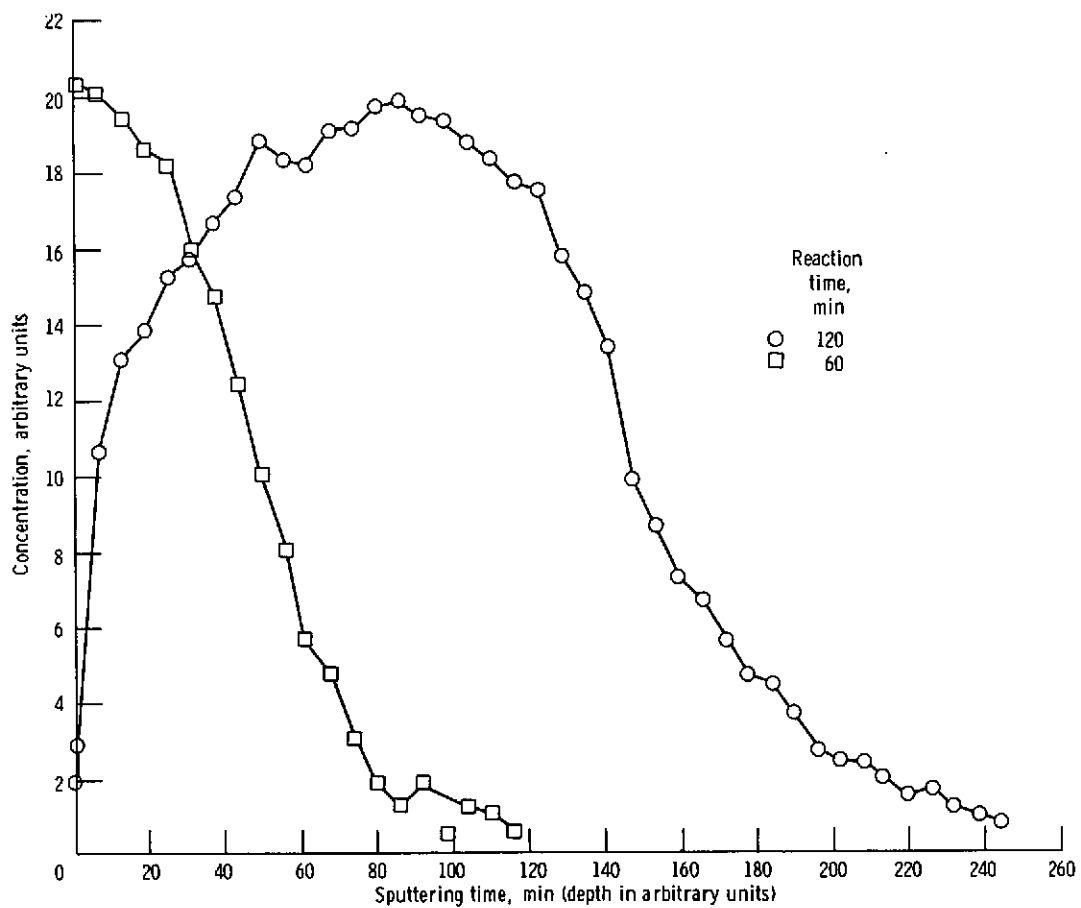


Figure 8. - Depth profile of oxygen concentration on a 440C surface following reaction with SO_2 at 500°C and 10^{-5} torr for 60 or 120 minutes.

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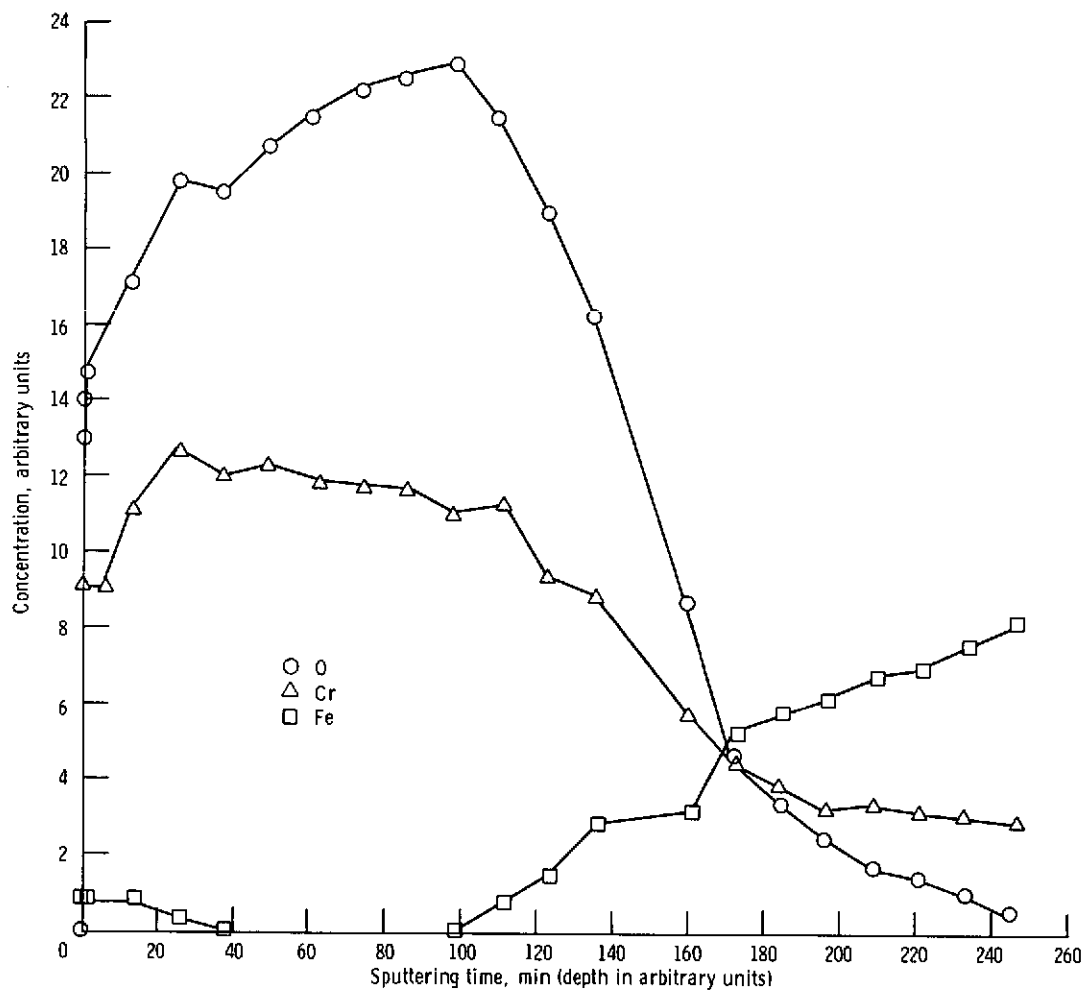


Figure 9. - Depth profile of 440C surface following reaction with SO_2 at 600°C and 10^{-5} torr for 30 minutes.

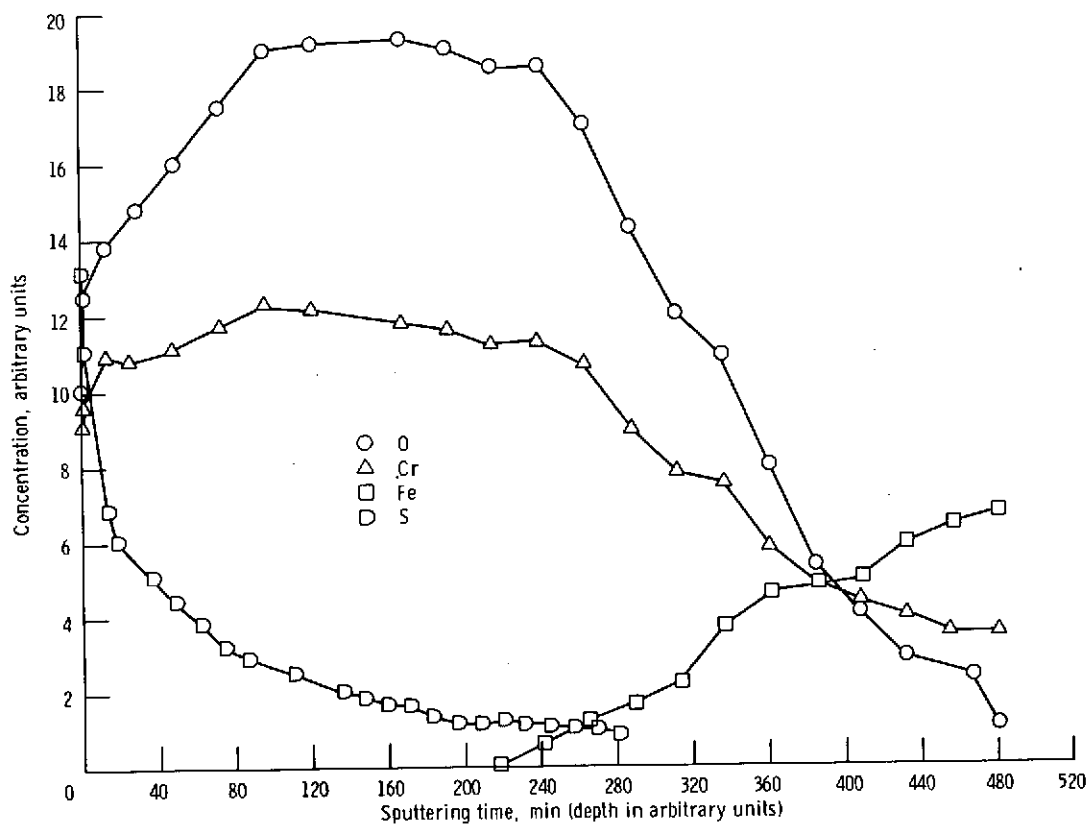


Figure 10. - Depth profile of 440C surface following reaction with SO_2 at 600°C and 10^{-5} torr for 60 minutes.

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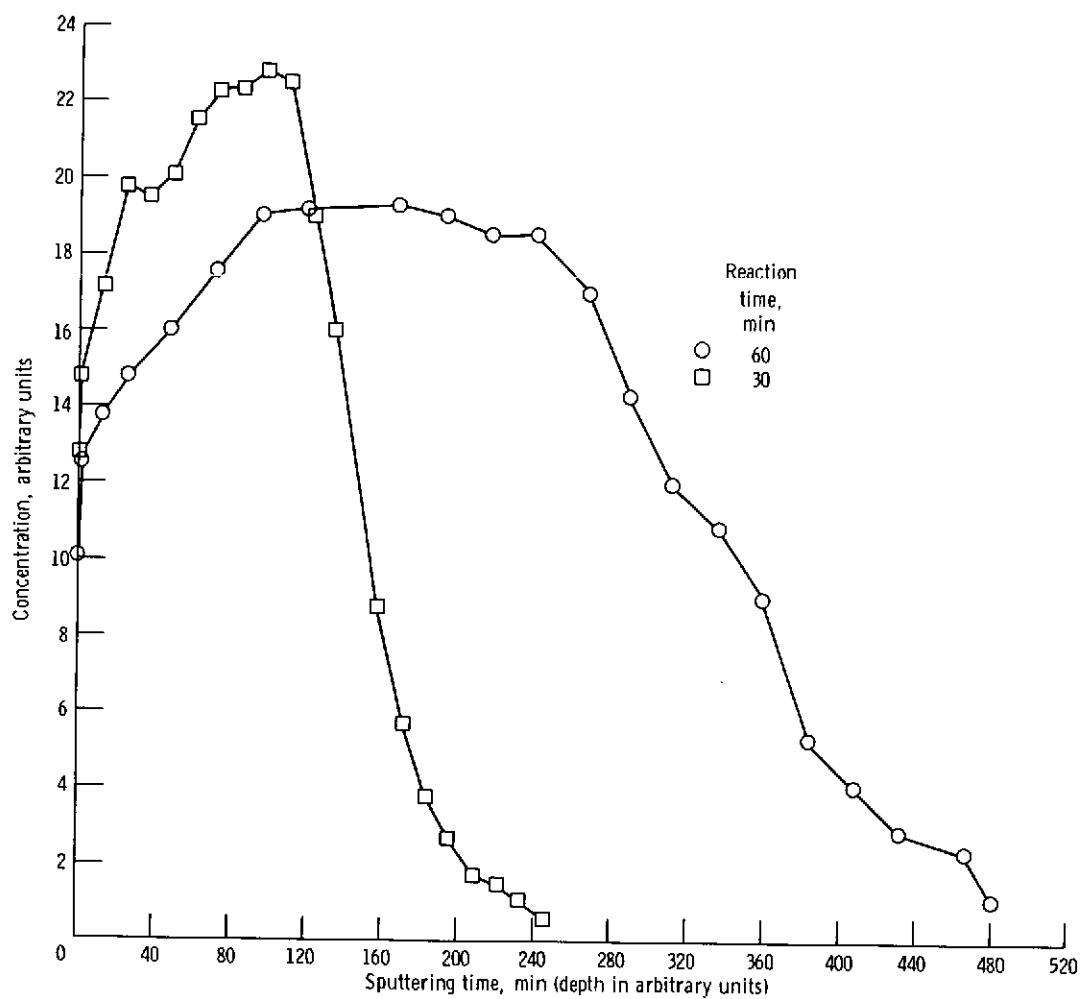


Figure 11. - Depth profile of oxygen concentration on a 440C surface following reaction with SO_2 at 600°C and 10^{-5} torr for 30 or 60 minutes.

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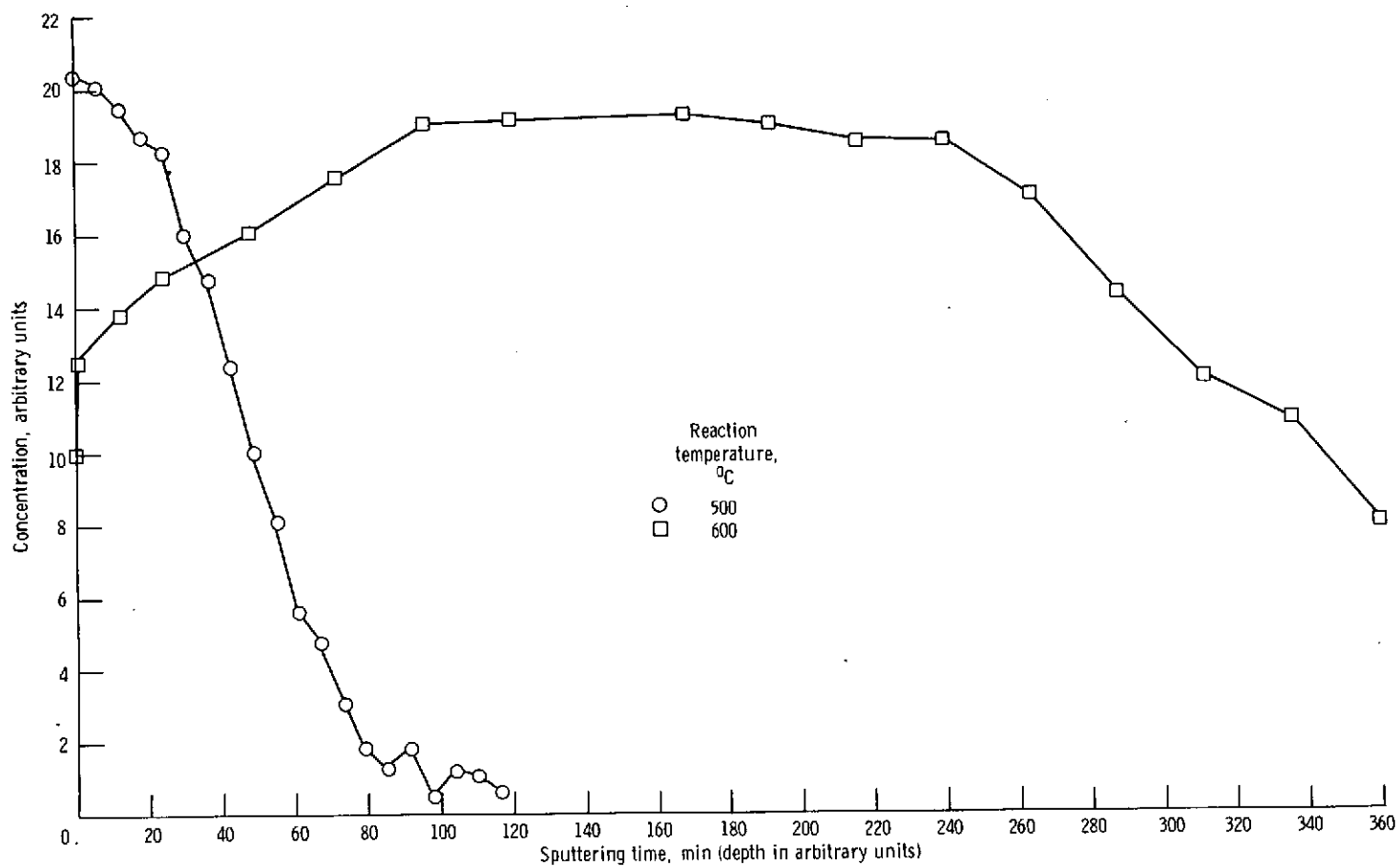


Figure 12 - Depth profile of oxygen concentration on a 440C surface for reactions with SO_2 at the same pressure (10^{-5} torr) and for the same time (1 hr) but at two different temperatures (500° and 600° C), showing effect of temperature on film thickness.